Supplementary Information

Water Uptake in Biochars: The Roles of Porosity and Hydrophobicity

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Materials and Methods (SI)

(i) PAS-FTIR

Prior to analysis by PAS-FTIR, samples were oven-dried, placed in sample cups, purged under a Helium flow for 10 s prior to analysis, and then scanned from wavenumber 400 to 4000 cm^{-1} with a resolution of 4 wavenumbers. Spectral data are presented after smoothing and baseline correction. Peaks were assigned in accordance with Keiluweit et al. [1].

(ii) Water and Ethanol Uptake Experiments

Biochar samples were packed into PVC sample cores using a standard weight packing protocol. The packing protocol consisted of 1) Add biochar to samples cores until ~1/2 full, then drop 200 g weight from ~15 cm onto biochar 3 times; 2) Add additional biochar to sample cores until ~3/4 full, then drop 200 g weight from ~15 cm onto biochar 3 times; 3) Add additional biochar slightly above top of sample core using empty core above as guide, then drop 200 g weight from ~15 cm onto biochar 6 times; 4) Use straight edge to remove excess biochar above top of sample core.

Relative humidity measurements were taken after the uptake experiment for a duration of 21 days using a Vaisala (Vantaa, Finland) HMP 35C probe connected to a Campbell Scientific (Logan, UT) CR10x data logger. These data indicated the relative humidity of the laboratory fluctuated between 40% and 55%. This likely allowed uptake of some water vapor by untreated samples prior to submersion in liquid water.

Results and Discussion (SI)

(i) Basic Properties

The positive correlation between pH, ash content, and electrical conductivity corroborates previous findings that pH in chars is primarily a function of alkaline salt abundance rather that the presence or absence of organic acids or bases [2]. Similar ash content between feedstocks but greater electrical conductivity in HZ chars compared to DF chars suggests that DF chars may contain more insoluble oxides in ash, as previously proposed to explain inconsistencies between manure chars [3].

(ii) Relative Humidity Treatments

We hypothesized that pretreating biochar with exposure to 100% relative humidity prior to submersion in water would increase water uptake compared to untreated chars. Although the pretreatment did not impact final uptake of liquid water (Figure S-4), there was substantial water vapor uptake by pretreated samples prior to submersion in liquid water (Table 2) confirming that the humidity pretreatment successfully pre-wetted samples. One reason for the lack of difference in liquid water uptake between the two treatments may be related to the hydraulic role of pyrogenic nanopores and the lack of total water saturation and hydraulic connectivity that can reasonably be obtained in submerged samples. Water vapor sorption in chars at high relative humidity is thought to occur primarily in pyrogenic nanopores [4], which may be hydraulically disconnected from liquid water entering residual macropores (Figure 2), thus conferring no benefit to liquid water uptake. Indeed, results indicated no difference in total water uptake between treatments and greater initial water uptake rates in untreated samples compared to humidity pretreated samples, suggesting that water taken up via vapor sorption was in fact hydraulically disconnected from liquid water entering biochar porosity. In general, results from this pretreatment experiment indicate that humid environments are not likely to improve the water uptake properties of biochars.

References (SI)

[1] Keiluweit M, Nico PS, Johnson MG, Kleber M. Dynamic molecular structure of plant biomass-derived black carbon (biochar). Environ Sci Technol 2010;44(4):1247–53.

[2] Yuan J-H, Xu R-K, Zhang H. The forms of alkalis in the biochar produced from crop residues at different temperatures. Bioresource Technol 2011;102(3):3488–97.

[3] Cantrell KB, Hunt PG, Uchimiya M, Novak JM, Ro KS. Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar. Bioresource Technol 2012;107:419–28.

[4] Pastor-Villegas J, Meneses Rodriguez JM, Pastor-Valle JF, Rouquerol J, Denoyel R, Garcia Garcia M. Adsorption-desorption of water vapour on chars prepared from commercial wood charcoals, in relation to their chemical composition, surface chemistry and pore structure. J Anal Appl Pyrol 2010;88(2):124–33.